

APPLICATION  
FOR  
UNITED STATES LETTERS PATENT

TITLE: ION TEXTURING METHODS AND ARTICLES  
APPLICANT: LESLIE G. FRITZEMEIER AND JOHN D. SCUDIERE

CERTIFICATE OF MAILING BY EXPRESS MAIL

Express Mail Label No. EL485713195US

I hereby certify under 37 CFR §1.10 that this correspondence is being deposited with the United States Postal Service as Express Mail Post Office to Addressee with sufficient postage on the date indicated below and is addressed to the Commissioner for Patents, Washington, D.C. 20231.

Date of Deposit

July 30, 2001

Signature

Typed or Printed Name of Person Signing Certificate

## **ION TEXTURING METHODS AND ARTICLES INCORPORATION BY REFERENCE**

The following documents are hereby incorporated by reference: U.S. Patent No. 5,231,074, issued on July 27, 1993, and entitled "Preparation of Highly Textured Oxide Superconducting Films from MOD Precursor Solutions," U.S. Patent No. 6,022,832, issued February 8, 2000, and entitled "Low Vacuum Process for Producing Superconductor Articles with Epitaxial Layers," U.S. Patent No. 6,027,564, issued February 22, 2000, and entitled "Low Vacuum Process for Producing Epitaxial Layers," U.S. Patent No. 6,190,752, issued February 20, 2001, and entitled "Thin Films Having Rock-Salt-Like Structure Deposited on Amorphous Surfaces," PCT Publication No. WO 00/58530, published on October 5, 2000, and entitled "Alloy Materials," PCT Publication No. WO/58044, published on October 5, 2000, and entitled "Alloy Materials," PCT Publication No. WO 99/17307, published on April 8, 1999, and entitled "Substrates with Improved Oxidation Resistance," PCT Publication No. WO 99/16941, published on April 8, 1999, and entitled "Substrates for Superconductors," PCT Publication No. WO 98/58415, published on December 23, 1998, and entitled "Controlled Conversion of Metal Oxyfluorides into Superconducting Oxides," PCT Publication No. WO 01/11428, published on February 15, 2001, and entitled "Multi-Layer Articles and Methods of Making Same," PCT Publication No. WO 01/08232, published on February 1, 2001, and entitled "Multi-Layer Articles And Methods Of Making Same," PCT Publication No. WO 01/08235, published on February 1, 2001, and entitled "Methods And Compositions For Making A Multi-Layer Article," PCT Publication No. WO 01/08236, published on February 1, 2001, and entitled "Coated Conductor Thick Film Precursor", PCT Publication No. WO 01/08169, published on February 1, 2001, and entitled "Coated Conductors With Reduced A.C. Loss" PCT Publication No. WO 01/15245, published on March 1, 2001, and entitled "Surface Control Alloy Substrates And Methods Of Manufacture Therefor," PCT Publication No. WO 01/08170, published on February 1, 2001, and entitled "Enhanced Purity Oxide Layer Formation," PCT Publication No. WO 01/26164, published on April 12, 2001, and entitled "Control of Oxide Layer Reaction Rates," PCT Publication No. WO 01/26165, published on April 12, 2001, and entitled "Oxide Layer Method," PCT Publication No. WO 01/08233, published on February 1,

2001, and entitled "Enhanced High Temperature Coated Superconductors," PCT Publication No. WO 01/08231, published on February 1, 2001, and entitled "Methods of Making A Superconductor," U.S. Patent Application Serial No. 09/579,193, filed on May 26, 2000, and entitled, "Oxide Bronze Compositions And Textured Articles Manufactured In Accordance Therewith," U.S. Patent Application Serial No. 09/694,400, filed on October 23, 2000, and entitled "Precursor Solutions and Methods of Using Same," and U.S. Patent Application Serial No. 09/ 855,312, filed on May 14, 2001, and entitled "Precursor Solutions and Methods of Using Same."

### **TECHNICAL FIELD**

The invention relates to ion texturing methods and articles.

### **BACKGROUND**

Multi-layer articles can be used in a variety of applications. For example, superconductors, including oxide superconductors, can be formed of multi-layer articles. Typically, such superconductors include a layer of superconductor material and a layer, commonly referred to as a substrate, that can enhance the mechanical strength of the multi-layer article.

Generally, in addition to enhancing the strength of the multi-layer superconductor, the substrate should exhibit certain other properties. For example, the substrate should have a low Curie temperature so that the substrate is not ferromagnetic at the superconductor's application temperature. Furthermore, chemical species within the substrate should not be able to diffuse into the layer of superconductor material, and the coefficient of thermal expansion of the substrate should be about the same as the superconductor material. Moreover, if the substrate is used for an oxide superconductor, the substrate material should be relatively resistant to oxidation.

For some materials, such as yttrium-barium-copper-oxide (YBCO), the ability of the material to provide high transport current in its superconducting state depends upon the crystallographic orientation of the material. For example, such a material can exhibit a relatively high critical current density ( $J_c$ ) when the surface of the material is biaxially textured.

As used herein, "biaxially textured" refers to a surface for which the crystal grains are in close alignment with a direction in the plane of the surface or in close alignment

with both a direction in the plane of the surface and a direction perpendicular to the surface. One type of biaxially textured surface is a cube textured surface, in which the primary cubic axes of the crystal grains are in close alignment with a direction perpendicular to the surface and with the direction in the plane of the surface. Examples of cube textured surfaces include the (100)[001] and (100)[011] surfaces, and an example of a biaxially textured surface is the (113)[211] surface.

For certain multi-layer superconductors, the layer of superconductor material is an epitaxial layer. As used herein, "epitaxial layer" refers to a layer of material whose crystallographic orientation is derived from the crystallographic orientation of the surface of a layer of material onto which the epitaxial layer is deposited. For example, for a multi-layer superconductor having an epitaxial layer of superconductor material deposited onto a substrate, the crystallographic orientation of the layer of superconductor material is derived from the crystallographic orientation of the substrate. Thus, in addition to the above-discussed properties of a substrate, it can be also desirable for a substrate to have a biaxially textured surface or a cube textured surface.

Some substrates do not readily exhibit all the above-noted features, so one or more intermediate layers, commonly referred to as buffer layers, can be disposed between the substrate and the superconductor layer. The buffer layer(s) can be more resistant to oxidation than the substrate, and reduce the diffusion of chemical species between the substrate and the superconductor layer. Moreover, the buffer layer(s) can have a coefficient of thermal expansion that is well matched with the superconductor material.

In some instances, a buffer layer is an epitaxial layer, so its crystallographic orientation is derived from the crystallographic orientation of the surface onto which the buffer layer is deposited. For example, in a multi-layer superconductor having a substrate, an epitaxial buffer layer and an epitaxial layer of superconductor material, the crystallographic orientation of the surface of the buffer layer is derived from the crystallographic orientation of the surface of the substrate, and the crystallographic orientation of the layer of superconductor material is derived from the crystallographic orientation of the surface of the buffer layer. Therefore, the superconducting properties exhibited by a multi-layer superconductor having a buffer layer can depend upon the crystallographic orientation of the buffer layer surface.

In certain instances, a buffer layer is not an epitaxial layer but can be formed using ion beam assisted deposition. Typically, ion beam assisted deposition involves exposing a surface to ions directed at a specific angle relative to the surface while simultaneously depositing a material. In instances where ion beam assisted deposition is used to form a buffer layer, the crystallographic orientation of the surface of the buffer layer can be unrelated to the crystallographic orientation of the surface of the underlying layer (e.g., a substrate). Generally, however, the ion beam deposition parameters such as, for example, the ion energy and beam current, the temperature, the ratio of the number of atoms arriving at the surface relative to the number of ions coincidentally arriving at the surface, and the angle of incidence on the surface are selected so that the crystallographic orientation of the surface of the buffer layer provides an appropriate template for a layer that is deposited on the surface of the buffer layer (e.g., a layer of superconducting material).

### SUMMARY

The invention generally relates to ion texturing methods and articles.

In part, the invention relates to ion texturing a nontextured surface while exposing the surface to one or more reactive species (e.g., nitrogen and/or oxygen) to form a textured surface having a different chemical composition than the nontextured surface. For example, the surface of a nitride can be exposed to ions and oxygen simultaneously to form a textured oxide surface. In certain embodiments, after ion texturing the surface, the surface can be exposed to one or more reactive species (e.g., nitrogen and/or oxygen) to modify the chemical composition of the textured surface. For example, an ion textured nitride surface can be exposed to oxygen to form a textured oxide surface.

In certain embodiments, multiple ion beams (e.g., two, three, four, etc.) can be used during ion texturing to texture a surface (e.g., a noncrystalline surface) of a layer of material (e.g., a layer of an already deposited material, such as an already deposited buffer layer) so that the surface of the material has a predetermined crystallographic orientation. The crystallographic orientation of the ion textured surface can be different than the natural growth orientation of the layer of material.

The surface to be textured can be, for example, that of a substrate, a buffer layer, a protective layer or a layer of superconductor material. In certain embodiments, a multi-

layer article (e.g., a multi-layer superconductor article, such as a coated superconductor article) can include more than one layer having an ion textured (or at least partially ion textured surface).

Materials that can be ion textured include, for example, metals, alloys, oxides of metals, nitrides of metals, oxides of alloys and nitrides of alloys. Such materials include, for example, nickel, nickel alloys, silver, MgO, titanium nitride, zirconia, zirconium nitride,  $TbO_x$ ,  $GaO_x$ , ceria ( $CeO_2$ ), yttria stabilized zirconia (YSZ),  $Y_2O_3$ ,  $LaAlO_3$ ,  $SrTiO_3$ ,  $Gd_2O_3$ ,  $LaNiO_3$ ,  $LaCuO_3$ ,  $SrRuO_3$ ,  $NdGaO_3$ , ruthenium oxide, barium titanate, lanthanum gallate, indium oxide and  $NdAlO_3$ .

In some embodiments, multiple ion beams can be used, and the combination of appropriate parameters (e.g., the angle of the ion beams relative to the surface normal, the angle of the ion guns relative to each other and/or the crystal structure of the layer of material exposed to the ion beams) can be used to provide the predetermined crystallographic orientation of the surface in a relatively short period of time.

The multiple ion beams can be simultaneously active, or the multiple ion beams can be used in sequence. In some embodiments, some or all of the ion beams can be simultaneously active for a portion of the ion bombardment, and some or all of the ion beams can be used sequentially for a portion of the ion bombardment.

In some embodiments, the multiple ion beams can provide an ion flux sufficiently high so that the sputtering rate of the noncrystalline surface would exceed the atom arrival rate during certain vapor deposition processes.

In certain embodiments, the process can provide a noncrystalline substrate having an ion textured surface.

In some embodiments, the process can provide a substrate with a noncrystalline layer deposited thereon. The surface of the noncrystalline layer can be ion textured.

In certain embodiments, the process can provide a substrate with one or more buffer layers (crystalline or noncrystalline, and/or epitaxial or nonepitaxial) with a layer (e.g., a thin protective layer) deposited thereon. The surface of the layer (e.g., protective layer) can be ion textured. The layer can act as a protective layer for one or more (e.g., all) of the underlying layers. The layer can be chemically compatible with a superconductor material or a precursor thereof (e.g., chemically compatible with a

halogen-containing precursor of YBCO, such as a fluoride-containing precursor, including one or more  $\text{BaF}_2$ -containing precursors).

In one aspect, the invention features a method that includes exposing a surface region of a layer of a first material having a first chemical composition to at least one ion beam (e.g., one ion beam, two ion beams, three ion beams, four ion beams, more than four ion beams) in an environment containing a reactive species to texture the surface region of the layer and to change the composition of the layer in the surface region to a second material having a second chemical composition different than the first chemical composition.

The reactive species can be, for example, oxygen and/or nitrogen.

The surface region can have a depth of less than about 50 nanometers. The depth of the surface region can be at least about five nanometers.

The first material can be a nitride, and the second material can be an oxide.

The first material can be, for example, vanadium nitride, zirconium nitride, titanium nitride or cerium nitride.

The second material composition can be, for example, vanadium oxide, zirconium oxide, titanium oxide or cerium oxide.

Prior to exposure to the at least one ion beam, the surface region can be noncrystalline.

After exposure to the at least one ion beam, the surface region can be textured.

The at least two ion beams can impinge on the surface region of the layer at a first angle relative to a perpendicular to the surface of the layer, and the at least two ion beams can be disposed relative to each other at a second angle so that the textured surface region has a crystal plane that is oriented perpendicular to the textured surface.

The method can further include exposing the second material to a reactive species in the absence of the at least two ion beams.

The second material can be exposed to the reactive species in the absence of the at least two ion beams at a temperature greater than room temperature.

In another aspect, the invention features a method of ion texturing a noncrystalline surface of a layer of a nitride. The method includes exposing a surface region of a layer of the nitride to at least two ion beams in an environment containing a

reactive species to texture the surface region of the layer and to change the composition of the layer in the surface region to an oxide to form a textured oxide surface.

The at least two ion beams can impinge on the surface region at a first angle relative to a perpendicular to the surface, and the at least two ion beams can be disposed relative to each other at a second angle so that a crystal plane of the textured surface region is oriented perpendicular to the textured oxide surface.

The reactive species can be, for example, oxygen.

The surface region of the oxide can have a depth of less than about 50 nanometers. The depth of the surface region of the oxide can be at least about five nanometers.

The nitride can be, for example, vanadium nitride, zirconium nitride, titanium nitride or cerium nitride.

The oxide can be, for example, vanadium oxide, zirconium oxide, titanium oxide or cerium oxide.

The method can further include exposing the second material to a reactive species in the absence of the at least two ion beams.

The oxide material can be exposed to the reactive species in the absence of the at least two ion beams at a temperature greater than room temperature.

The invention can provide superconductor articles having a relatively high critical current density (e.g., coated superconductor articles having a relatively high critical current density, such as a coated conductor having a layer of superconductor material with biaxial texture or cube texture) without using a textured substrate (e.g., by using a noncrystalline substrate, such as a substrate having an amorphous surface or a polycrystalline surface).

The invention can provide superconductor articles having a relatively high critical current density (e.g., coated superconductor articles having a relatively high critical current density) without epitaxially growing a layer on the surface of a substrate.

The invention can provide superconductor articles having a relatively high critical current density (e.g., coated superconductor articles having a relatively high critical current density) with relatively few epitaxially grown layers (e.g., with only the layer of superconductor material being epitaxially grown).



The invention can provide relatively fast methods of growing a textured layer of material (e.g., a textured buffer layer of a superconductor article, such as a coated superconductor article).

The invention can provide methods of preparing a textured (e.g., highly textured) layer of material (e.g., a buffer layer of a superconductor article, such as a coated superconductor article) without growing the layer of material epitaxially.

The invention can provide methods of exposing a layer of material (e.g., a noncrystalline material, such as an amorphous material or a polycrystalline material) to ions to texture (e.g., highly texture) the material (e.g., to texture at least a region of the material adjacent a surface of the material exposed to ion texturing).

The invention can provide methods of preparing a superconductor article (e.g., a superconductor article having a relatively high critical current density), such as a coated superconductor article, in which a relatively stable layer (e.g., a layer of ceria ( $\text{CeO}_2$ )) is used so that subsequent layer(s) (e.g., a layer of a superconductor material) can be incorporated (e.g., disposed) under different environmental conditions and/or after a relatively long period of time following formation of the layer (e.g., a buffer layer, such as a buffer layer having an ion textured surface) underlying the relatively stable layer.

The invention can provide methods of preparing a superconductor article (e.g., a superconductor article having a relatively high critical current density), such as a coated superconductor article, in which a layer of a superconductor material (e.g., YBCO) is disposed on a layer of a material (e.g., a layer of ceria) that is chemically compatible with the superconductor material and/or one or more precursor(s) of the superconductor material (e.g., a barium-containing precursor, such as a precursor containing  $\text{BaF}_2$ ). Generally, the layer of the chemically compatible material has a textured surface on which the layer of the superconductor material is disposed. The layer of chemically compatible material can be, for example, epitaxially grown, grown by ion beam assisted deposition, or prepared using ion texturing. Combinations of these methods can be used.

The invention can provide methods of ion texturing a layer (e.g., a layer of a superconductor article, such as a coated superconductor article) without concern for the ion to atom ratio used during ion bombardment.

The invention can provide methods of ion texturing relatively rough surfaces because the use of multiple ion beams can overcome shadowing effects.

The invention can provide methods of ion texturing that can overcome the natural growth orientation of the material of interest (i.e., the growth orientation of the material of interest in the absence of multiple ion beams). This can allow for the predetermined selection of the crystal plane that is oriented parallel to the ion textured surface.

The use of multiple (e.g., two, three, four, etc.) ion beams can reduce certain undesirable effects associated with ion beam divergence. In some embodiments, this can result in improved surface quality.

Features, objects and advantages of the invention are in the description, drawings and claims.

### DESCRIPTION OF DRAWINGS

Fig. 1 is a cross-sectional view of an embodiment of a multi-layer article;

Fig. 2A is a side view of an embodiment of a system having two ion beam sources;

Fig. 2B is a perspective view of an embodiment of a system having two ion beam sources;

Fig. 3A is a side view of an embodiment of a system having three ion beam sources;

Fig. 3B is a perspective view of an embodiment of a system having three ion beam sources;

Fig. 4A is a side view of an embodiment of a system having four ion beam sources;

Fig. 4B is a perspective view of an embodiment of a system having four ion beam sources;

Fig. 5 is a cross-sectional view of an embodiment of a multi-layer article; and

Fig. 6 is a cross-sectional view of an embodiment of a multi-layer article.

## DETAILED DESCRIPTION

Fig. 1 shows a multi-layer article 10 (e.g., a superconductor article) including a layer 12 (e.g., a substrate) with a surface 13, a layer 16 (e.g., a buffer layer) with an ion textured surface 17, and a layer 14 (e.g., a layer of a superconductor material) with a surface 15. Layer 16 is disposed on surface 13, and layer 14 is disposed on ion textured surface 17.

Generally, prior to ion texturing, the surface of layer 16 is a noncrystalline form (e.g., an amorphous form or a nano-crystalline form). This noncrystalline surface is exposed to at least two ion beams to at least partially texture (e.g., fully texture) the surface, thereby forming ion textured surface 17 that has a predetermined orientation both in the plane of surface 17 and out of the plane of surface 17. In certain embodiments, the surface of layer 16 can be partially textured prior to ion texturing, and ion texturing can be used to achieve ion textured surface 17.

A noncrystalline (e.g., amorphous or nano-crystalline) surface generally exhibits no clear or distinct diffraction peaks in a conventional x-ray  $\theta$ - $2\theta$  scan. Typically, the signal in a conventional x-ray  $\theta$ - $2\theta$  scan of a noncrystalline surface is less than about 10% of the corresponding signal in a conventional x-ray  $\theta$ - $2\theta$  scan of a crystalline surface when the signal is measured at a point in the respective x-ray  $\theta$ - $2\theta$  scans corresponding to a characteristic peak for the crystalline surface.

Ion textured surface 17 can be, for example, biaxially textured (e.g., cube textured) with the (111), (001) or (110) planes oriented perpendicular to the surface 17, and surface 17 can have a specific crystalline direction (e.g., (100)) oriented in the plane with respect to the ion beams.

Figs. 2A and 2B show a side view and a perspective view, respectively, of an embodiment of an ion texture system 20 for ion texturing surface 17. System 20 includes two ion beam sources (e.g., ion beam guns, such as three centimeter Commonwealth Scientific ion guns) 22 and 24 that direct ion beams 26 and 28, respectively, at surface 17. Ion beams 26 and 28 are directed at surface 17 at an angle  $\theta$  relative to a perpendicular 21 of surface 17. Ion beams 26 and 28 are also directed with respect to each other at an angle  $\alpha$ .

Without wishing to be bound by theory, it is believed that multiple ion beams can operate together to ion texture a noncrystalline surface, resulting in a surface with an improved level of in-plane and out-of-plane orientation control. It is believed that, using only one ion beam, only one crystallographic direction is preferred to align with the ion beam, and the crystal can be oriented in random rotational aspects relative to this direction. It is also believed that a second ion beam can be used to reinforce the crystallization process, provided that: 1.) the ion beams are at appropriate angle  $\theta$  relative to the perpendicular of the noncrystalline surface; and 2.) the ion beams are at an appropriate angle  $\alpha$  relative to each other. It is further believed that additional ion beams (e.g., a third ion beam, a fourth ion beam, etc.) located at an appropriate angle  $\alpha$  relative to the other ion beams can additionally enhance the in-plane and out-of-plane alignment of the ion textured surface.

The angle  $\alpha$  is generally determined by the crystal structure of the material of layer 16 and the desired orientation of surface 17 subsequent to ion texturing, and the angle  $\alpha$  is typically chosen so that each of ion beams 26 and 28 is aligned along the same equivalent crystallographic direction.

For example, materials with cubic structures (e.g., a rock salt structure material such as MgO, TiN, CaO, SrO, ZrO or BaO, or a fluorite structure material, such as yttria stabilized zirconia (YSZ) or ceria) exhibit four fold symmetry so that each crystalline direction is repeated four times within the crystal unit. The angle  $\alpha$  between two equivalent crystallographic directions is readily determined by standard geometrical calculations and/or tables of interplanar angles. Information regarding appropriate values for  $\alpha$  is disclosed, for example, in J.W. Edington, Practical Electron Microscopy in Materials Science, Van Nostrand Rheinhold Company, 1976, which is hereby incorporated by reference.

As another example, materials with hexagonal structures (e.g., titanium, yttrium, zirconium, BaTiO<sub>3</sub>, TiB<sub>2</sub>) exhibit 6-fold symmetry so that each crystalline direction is repeated six times within the crystal unit. The angle  $\alpha$  is determined for hexagonal materials in a manner similar to that described for cubic materials.

The angle  $\theta$  is generally selected so that each of ion beams 26 and 28 is maintained along a specific crystallographic orientation and so that ion texturing

produces the desired texture (e.g., biaxial texture or cube texture) in surface 17. Each of ion beams 26 and 28 can be at a different angle  $\theta$  with respect to the perpendicular of surface 17. Alternatively, each of ion beams 26 and 28 can be at the same angle  $\theta$  with respect to the perpendicular of surface 17.

For example, in embodiments in which layer 16 is formed of YSZ and in which a cube textured surface is desired, the angle  $\theta$  would be about  $54.7^\circ$  to conform with crystallographic requirements. Those skilled in the art will recognize that in practical applications this angle can be from about  $51^\circ$  to about  $59^\circ$  (e.g., from about  $53^\circ$  to about  $57^\circ$ , about  $55^\circ$ ,  $54.7^\circ$ ). As another example, in embodiments in which layer 16 is formed of ceria or MgO,  $\theta$  can similarly be from about  $40^\circ$  to about  $50^\circ$  (e.g., from about  $43^\circ$  to about  $47^\circ$ , about  $45^\circ$ ).

While certain values for  $\theta$  and  $\alpha$  have been disclosed, other values will be apparent to those skilled in the art. For example, values for  $\theta$  and/or  $\alpha$  can be determined from information available from ion beam assisted deposition studies and from available crystal structure information, such as disclosed, for example, in J.W. Edington, Practical Electron Microscopy in Materials Science, Van Nostrand Rheinhold Company, 1976.

The appropriate parameters for ion texturing have been generally discussed above with particular reference to an ion texture system containing two ion guns. It is to be understood, however, that the general principles for appropriate parameter selection for ion texturing a noncrystalline surface which are discussed above can be applied to ion texture systems containing more than two ion guns.

For example, Figs. 3A and 3B show a side view and a perspective view, respectively, of an ion texture system 80 containing ion guns 22, 24 and 50 having ion beams 26, 28 and 51, respectively. Ion gun 50 is configured at an angle  $\alpha'$  relative to ion guns 22 and 24, and ion guns 22 and 24 are configured at an angle  $\alpha$  relative to each other. Angles  $\alpha$  and  $\alpha'$  correspond to the angles between equivalent crystallographic directions in the crystal of interest. Each of ion beams 26, 28 and 52 are configured at angle  $\theta$  with respect to perpendicular 21.

As another example, Figs. 4A and 4B show a side view and a perspective view, respectively, of an ion texture system 90 containing ion guns 22, 24, 50 and 52 having ion beams 26, 28, 51 and 53, respectively. Each of ion guns 50 and 52 is configured at an

angle  $\alpha'$  relative to ion guns 22 and 24, and ion guns 22 and 24 are configured at an angle  $\alpha$  relative to each other. Angles  $\alpha$  and  $\alpha'$  correspond to the angles between equivalent crystallographic directions in the crystal of interest. Each of ion beams 26, 28, 50 and 52 are configured at angle  $\theta$  with respect to perpendicular 21.

It is to be understood that, while the foregoing description has involved simultaneous use of ion guns, multiple ion guns need not be used simultaneously to ion texture a noncrystalline surface. For example, multiple ion guns may be used in sequence. As another example, multiple ion guns may be used simultaneously for a portion of the ion texturing process, and in sequence in another part of the ion texturing process. As a further example, certain ion guns may be used simultaneously during ion texturing, while other ion guns are used in sequence.

It is also to be understood that ion texturing can be used in combination with ion beam assisted deposition. For example, a layer can be formed using ion beam assisted deposition, and subsequently textured using ion texturing. This can be desirable, for example, when ion beam assisted deposition can be used to deposit the material relatively quickly (e.g., when growing certain oxides and/or certain nitrides). Alternatively or additionally, a surface can be partially (or even fully) textured using ion texturing, followed by ion beam assisted deposition (e.g., to complete formation of the layer of material with the surface of the completed layer having, for example, a fully textured surface or a partially textured surface). This can be desirable, for example, to enhance the texture of the material. Combining a step of ion texturing followed by ion beam assisted deposition can reduce the ion beam assisted deposition time for achieving a particular material layer having a desired amount of surface texture.

It is to be further understood that, while the figures show certain directions of the ion beams relative to each other directions can be chosen based upon the crystallography of the material to be ion textured and based upon the desired biaxial surface texture to be achieved. The technique can be generalized to provide a surface texture which supports the desired functionality of the article.

In general, ion texturing can be performed under any temperature that results in the desired surface texture (e.g., the desired in-plane and out-of-plane alignment). Typically, when ion texturing surface 17, layer 16 is at a temperature above room

temperature. Generally, when ion texturing surface 17, layer 16 is a temperature below the crystallization temperature of the material from which layer 16 is formed (e.g., a temperature below but near the crystallization temperature of the material from which layer 16 is formed). In some embodiments, when ion texturing surface 17, layer 16 is at a temperature below the temperature at which the material from which layer 16 is formed will undergo crystallization without the assistance of the ions. In certain embodiments, the temperature of layer 16 during ion texturing of surface 17 can be up to about one third the melting point of the material from which layer 16 is formed. In embodiments in which layer 16 is formed of YSZ, ceria or MgO, the temperature of layer 16 during ion texturing of surface 17 can be up to, for example, about 900°C.

Generally, surface 17 is exposed to the ion beams for a period of time sufficient to result in surface 17 having the desired texture (e.g., the desired in-plane and out-of-plane alignment). In some embodiments, ion texturing is performed for at least about 10 seconds (e.g., at least about one minute, at least about five minutes, at least about 10 minutes, at least about 30 minutes, from about one minute to about 10 minutes, from about three minutes to about seven minutes, from about four minutes to about six minutes).

In certain embodiments, after surface 17 has been textured (or at least partially textured) by ion beams 26 and 28, the temperature of layer 16 can be decreased (e.g., to about room temperature) while continuing to expose surface 17 to ion beams 26 and/or 28 (e.g., with or without changing the ion flux of beams 26 and/or 28). It is believed that this can assist in maintaining the desired texture of surface 17 (e.g., the in-plane and out-of-plane alignment of surface 17) while the temperature of layer 16 is decreased (e.g., to about room temperature).

Typically, ion texturing is performed in an environment of reduced total pressure (e.g., a pressure less than about 10 milliTorr, less than about one milliTorr, from about 0.1 milliTorr to about one milliTorr, from about 0.5 milliTorr to about one milliTorr).

Generally, surface 17 can be exposed to the ion beams in any environment that allows for the desired texturing of surface 17 (e.g., the desired in-plane and out-of-plane alignment). In certain embodiments, the environment includes one or more inert gases (e.g., He, Ne, Ar, Kr and/or Xe) and/or one or more types of neutral particles. In some

embodiments, one or more of the ion beams contain one or more reactive species (e.g., oxygen and/or nitrogen). In certain embodiments, one or more of the ion beams include one or more inert gases and/or types of neutral particle, and one or more reactive species (e.g., an inert gas and a reactive species; a neutral particle and a reactive species. The ratio of the reactive specie(s) (e.g., oxygen) to inert gas(es) is at least about 1:1 (e.g., at least about 1:10, at least about 1:20).

The ions impinging on surface 17 should have sufficient energy to result in surface 17 having the desired texture (e.g., the desired in-plane and out-of-plane alignment). In certain embodiments, the energy of the ions is low enough to avoid undesired sputtering of the material from which layer 16 is formed. The ions typically have an energy of at least about 10 eV (e.g., at least about 100 eV, at least about 200 eV, at least about 300 eV, at most about 500 eV) and at most about 1,000 eV (e.g., at most about 900 eV, at most about 800 eV, at most about 700 eV, at most about 600 eV).

The flux of ions at surface 17 should be sufficient to result in surface 17 having the desired texture (e.g., the desired in-plane and out-of-plane alignment). In some embodiments, because the material from which layer 16 is formed is not being simultaneously deposited during ion bombardment, the flux of ions at surface 17 during ion texturing can be substantially higher than the flux of ions typically used during ion beam assisted deposition. For example, the flux of ions can be at least about 10 microAmperes per square centimeter (e.g., at least about 50 microAmperes per square centimeter, at least about 100 microAmperes per square centimeter, at least about 200 microAmperes per square centimeter, at least about 300 microAmperes per square centimeter, at least about 400 microAmperes per square centimeter, at least about 500 microAmperes per square centimeter, at least about 600 microAmperes per square centimeter, at least about 700 microAmperes per square centimeter, at least about 800 microAmperes per square centimeter, at least about 900 microAmperes per square centimeter, at least about 1,000 microAmperes per square centimeter).

In some embodiments, the ion texturing method textures the surface of layer 16 to a depth of less than about 50 nanometers (e.g., less than about 25 nanometers, less than about 20 nanometer). In certain embodiments, the ion texturing method textures layer 16



to a depth of at least about five nanometers (e.g., at least about 10 nanometers, at least about 15 nanometers).

Ion textured surface 17 typically can have a full width at half maximum (FWHM) X-ray phi scan value of less than about 20° (e.g., less than about 15°, less than about 10°, less than about 5°).

In some embodiments, ion textured surface 17 has a root mean square roughness of less than about 100 angstroms (e.g., less than about 50 angstroms, less than about 25 angstroms) as determined using atomic force microscopy or profilometry.

Noncrystalline layer 16 can be prepared using any of the standard methods for forming a noncrystalline layer. Such methods include, for example, chemical vapor deposition, physical vapor deposition, metalorganic deposition, or magnetron sputtering.

In some embodiments, noncrystalline layer 16 can be prepared relatively quickly (e.g., greater than about one nanometer per second, greater than about five nanometers per second, greater than about 10 nanometers per second).

In certain embodiments, layer 16 has a thickness of greater than about 20 nanometers (e.g., greater than about 50 nanometers, greater than about 100 nanometers, greater than about 500 nanometers, greater than about 750 nanometers). In some embodiments, layer 16 is less than about 1000 nanometers thick (e.g., less than about 800 nanometers thick, less than about 600 nanometers thick, less than about 400 nanometers thick).

Layer 16 can be formed of any material appropriate for use in article 10 (e.g., a buffer layer for a superconductor article). Such materials include, for example, metals, and metal oxides, such as silver, nickel, TbO<sub>x</sub>, GaO<sub>x</sub>, ceria, YSZ, Y<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3</sub>, SrTiO<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, LaNiO<sub>3</sub>, LaCuO<sub>3</sub>, SrRuO<sub>3</sub>, NdGaO<sub>3</sub>, NdAlO<sub>3</sub> and/or nitrides as known to those skilled in the art.

In some embodiments, the ion texturing process can be used to change the chemical composition, as well as the texture, of a portion of layer 16. One or more (e.g., two, three, four, more than four) ion beams (e.g., emitted by one or more ion beam sources) can be used. In these embodiments, one or more reactive species (e.g., oxygen and/or nitrogen) can be included in the ion beam environment to affect the change in chemical composition. The ion beam can further include one or more inert gases (e.g.,

He, Ne, Ar, Kr and/or Xe) and/or one or more types of neutral particles. The method can optionally include further exposure of the surface to the reactive species subsequent to ion texturing. This further exposure can occur at elevated temperature (e.g., greater than about room temperature, greater than about 50°C, greater than about 100°C, greater than about 200°C, greater than about 300°C, greater than about 400°C, greater than about 500°C). Preferably, the method results in at least a portion of layer 16 having a different chemical composition that is textured and that is thermodynamically stable relative to subsequent processing steps.

For example, a noncrystalline (e.g., amorphous or polycrystalline) layer of a nitride compound (e.g., vanadium nitride, zirconium nitride, titanium nitride or cerium nitride) can be exposed to ion beams 26 and 28 in an environment containing oxygen. The resulting layer can contain a portion of the noncrystalline nitride compound and a portion of the corresponding oxide (e.g., vanadium oxide, zirconia, titanium oxide or ceria, respectively) that is at least partially textured. Optionally, surface of layer 17 can be exposed to oxygen subsequent to ion bombardment (e.g., for further oxidation).

As another example, a noncrystalline (e.g., amorphous or polycrystalline) layer of a nitride compound (e.g., titanium nitride) can be exposed to ion beams 26 and 28 in an environment containing strontium and oxygen. The resulting layer can contain a portion of the noncrystalline nitride compound and a portion of the corresponding oxide (e.g., SrTiO<sub>3</sub>) that is at least partially textured. Optionally, the surface of layer 17 can be exposed to oxygen subsequent to ion bombardment (e.g., for further oxidation).

Alternatively, the chemical composition of an ion textured surface can be changed subsequent to ion bombardment without also changing the chemical composition during ion texturing. For example, a layer of a nitride compound (e.g., vanadium nitride, titanium nitride, cerium nitride or zirconium nitride) can be exposed to an environment containing one or more reactive species (e.g., oxygen) subsequent to ion texturing in an inert environment to change the chemical composition of at least a portion of the textured surface (e.g., to vanadium oxide, titanium oxide, ceria or zirconia, respectively).

Exposure to the reactive species can occur at elevated temperature.

In embodiments in which a portion of layer 16 is chemically changed (i.e., before or after ion texturing), the chemically changed portion (which can also be textured) of

layer 16 can have a depth of less than about 50 nanometers (e.g., less than about 25 nanometers, less than about 20 nanometer). The depth of the chemically changed portion of layer 16 can have a depth of at least about five nanometers (e.g., at least about 10 nanometers, at least about 15 nanometers).

These methods of modifying the chemical composition during or after ion texturing can be advantageous, for example, because nitrides can act as a better barrier to diffusion of chemical constituents of layer 12 to layer 16. These methods can also be advantageous, for example, when it is quicker to form the nitride compound (e.g., by ion beam assisted deposition) than the corresponding oxide compound so that this method is a relatively quick way of forming a textured oxide surface. These methods can be further advantageous, for example, because the nitride compound can be more resistant to chemical change. These methods can also be advantageous because the modified composition can be more stable than the initial composition of layer 16. The chemically stable ion textured surface 17 can then advance into layer 16 during subsequent exposure.

Layer 12 can be formed of any material capable of supporting layer 16. In embodiments in which article 10 is a multi-layer superconductor, layer 12 can be formed of a substrate material, such as a metal or alloy. In certain embodiments, layer 12 is formed of a mechanically strong, flexible material that is suitable for its intended application (e.g., suitable for use in an extended length coated superconductor in the shape of a tape).

Generally, layer 12 is not textured. Typically, layer 12 is polycrystalline or noncrystalline. In some embodiments in which layer 12 is polycrystalline or noncrystalline, surface 17 and/or surface 15 can be textured (e.g., biaxially textured or cube textured).

In some embodiments, layer 12 is formed of a metal or alloy having a coefficient of thermal expansion that is about the same as the coefficient of thermal expansion of the material of layers 14 and/or 16. In certain embodiments, layer 12 is formed of a material that is relatively stable against oxidation under the processing conditions to which it is exposed. An example of a material from which layer 12 can be formed is an alloy of Ni, Cr and Mo. The Cr can be used, for example, to form an oxide scale which is stabilized against both oxygen and cation diffusion by the addition of Mo. The oxide scale can be

thin, self-healing and/or provide good protection of layer 14 from the diffusion of constituents of layer 12 (this can allow layer 16 to be relatively thin, such as, for example, less than about 250 nanometers thick). In alternate embodiments, layer 12 can be formed of a metal oxide, such as YSZ.

In certain embodiments in which layer 12 is noncrystalline, surface 13 can be ion textured (e.g., when layer 12 is formed of YSZ, such as noncrystalline YSZ formed by, for example, tape casting and sintering). In these embodiments, layer 16 need not be present.

Other examples of materials (e.g., metals or alloys) that can be used for layer 12 are known to those skilled in the art and are contemplated as being within the scope of the invention.

Layer 14 can be formed of a superconductor material. Examples of superconductor materials include rare earth-barium-copper-oxides (REBCO), such as YBCO (e.g.,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ), bismuth-strontium-calcium-copper-oxides, thallium, and/or mercury based superconductors. A layer of superconductor material can be formed, for example, by pulsed laser deposition, chemical vapor deposition, physical vapor deposition, thermal evaporation, electron beam processes (e.g., using  $\text{BaF}_2$ ), direct electron beam growth, slurry processes, chemical methods, liquid phase epitaxy and/or spray pyrolysis.

In certain embodiments, a layer of superconductor material is prepared by disposing a superconductor precursor (e.g., a superconductor precursor solution) on ion textured surface 17 and subsequently processing the precursor to provide the superconductor material. Examples of such precursors include acids, such as acetic acids, including halogenated (e.g., fluorinated and/or chlorinated) acetic acids, including perhaloacetic acids (e.g., perfluoroacetic acid, perchloroacetic acid). Superconductor precursors and methods of processing such precursors to provide superconductor materials are known to those skilled in the art and are contemplated as being within the scope of the invention.

In certain embodiments, layer 14 has a relatively high critical current density (e.g., at least about  $5 \times 10^5$  Amperes per square centimeter, at least about  $1 \times 10^6$  Amperes per square centimeter, and at least about  $2 \times 10^6$  Amperes per square centimeter) as

determined by transport measurement at 77K in self field (i.e., no applied field) using a 1 microVolt per centimeter criterion.

In some embodiments, layer 14 is well-ordered (e.g., biaxially textured in plane, or c-axis out of plane and biaxially textured in plane).

The thickness of layer 14 can vary depending upon the intended purpose of article 10. In some embodiments, layer 14 preferably has a thickness of from about 1 micron to about 10 microns (e.g., from about 3 microns to about 8 microns, such as from about 4 microns to about 6 microns).

Fig. 5 shows an embodiment of an article 30 having layers 12, 14, 16 and 18. In article 30, surface 17 can be ion textured or non-ion textured. Layer 18 is disposed on surface 17 of layer 16, and layer 14 is disposed on ion textured surface 19 of layer 18.

In article 30, layer 18 can be formed of a material that is chemically compatible with the material of layer 14 or a precursor thereof. A material that is chemically compatible with the material of layer 14 or a precursor thereof is a material on which layer 14 can be formed without substantially changing the chemical and/or physical properties of the chemically compatible material. For example, in certain embodiments, such as when layer 14 is formed of a rare earth barium copper oxide (e.g., YBCO), layer 14 may be formed on layer 18 by a process that includes using a precursor that contains one or more halide-containing species (e.g., one or more fluoridic and/or chlorodic species, such as  $\text{BaF}_2$ ). In these embodiments, layer 18 should be formed of a material that is chemically compatible with layer 14 under the conditions used to process the precursor to form layer 14. In some embodiments, layer 18 is formed of ceria,  $\text{LaAlO}_3$ , or  $\text{SrTiO}_3$ .

In certain embodiments, surface 19 is textured (e.g., biaxially textured or cube textured) so that layer 14 can be epitaxially formed on surface 19. In some embodiments, surface 19 is ion textured.

In article 30, layer 16 can be thicker than layer 18. For example, layer 16 can have a thickness of at least about 0.1 microns (e.g., at least about 0.3 microns, from about 0.3 microns to about 0.7 microns, from about 0.4 microns to about 0.6 microns, about 0.5 microns). Layer 18 can be less than about 100 nanometers thick (e.g., less than about 50 nanometers thick, from about five nanometers to about 100 nanometers thick, from about

10 nanometers to about 75 nanometers thick, from about 20 nanometers to about 50 nanometers thick).

While certain structures of multi-layer articles (e.g., multi-layer superconductor articles) have been disclosed, other structure are also contemplated. For example, the number of layers (e.g., three layers, four layers, five layers, six layers, seven layers, etc.) disposed between a substrate and a layer of superconductor material can vary as desired. The surfaces of one or more of these layers can be ion textured. The chemical composition of these layers can be the same or different.

Superconductor articles according to the invention can also include a layer of a cap material disposed thereon. Fig. 6 shows an embodiment of such an article 60 having layers 12, 14, 16 and a cap layer 56. Cap layer 56 can be formed of a material (e.g., a metal or alloy) whose reaction products with the superconductor material (e.g.,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ) are thermodynamically unstable under the reaction conditions used to form the layer of cap material. Exemplary cap materials include silver, gold, palladium and platinum.

While the foregoing discussion has described multi-layer articles having certain structures, the invention is not limited in this sense. Examples of other structures are known to those skilled in the art and contemplated as being within the scope of the invention. Moreover, while methods mentioned above have referred to the use of ions, other particles can also be used (e.g., neutrons, neutral atoms and/or neutral molecules). Furthermore, in embodiments in which multiple intermediate material layers are present between the substrate and the layer of superconductor material, the intermediate layers can provide different desirable properties (e.g., one or more intermediate layers provide good resistance to diffusion of chemical species from the substrate to the layer of superconductor material; one or more intermediate layers are readily textured via ion texturing; one or more layers are chemically compatible with the superconductor material and/or precursors thereof). In some embodiments, this can be achieved by disposing the multiple intermediate layers in sequence. In certain embodiments, this can be achieved by changing the chemical composition of one or more layers of material during ion texturing.

The following examples are illustrative only and not intended to be limiting.

#### Example I

A (001)<100> YSZ surface is formed using two ion beams as follows.

Each of two ion beams is provided at an angle of about  $55^\circ$  to the perpendicular of a noncrystalline YSZ surface. The two ion beams are about  $110^\circ$  apart. Each ion gun is from about three to about five centimeters from the YSZ surface. This corresponds to the arrangement shown in Figs. 2A and 2B where  $\alpha$  is about  $110^\circ$  and  $\theta$  is about  $55^\circ$ . The surface of the noncrystalline YSZ material is heated to a temperature of from about  $700^\circ\text{C}$  to about  $800^\circ\text{C}$  after which the two ion guns are activated so that the surface of the noncrystalline YSZ material is simultaneously exposed to ions from the ion guns. The ion guns are operated at 300 eV each with a beam current of from about 10 microAmperes per square centimeter to about 100 microAmperes per square centimeter. Ion texturing is performed for a time period of from about 30 seconds to about 90 seconds. This results in a (001)<100> YSZ textured layer of about 20 nanometers in thickness and having a FWHM X-ray phi scan value of less than about  $10^\circ$ .

#### Example II

A (001)<100> YSZ surface is formed using two ion beams as follows.

The process of Example I is followed except that the two ion beams are about  $70.5^\circ$  apart. This corresponds to the arrangement shown in Figs. 2A and 2B where  $\alpha$  is about  $70.5^\circ$  and  $\theta$  is about  $55^\circ$  for both ion beams.

#### Example III

A (001)<100> YSZ surface is formed using three ion beams as follows.

The process of Example I is followed except that a third ion gun is provided at an angle of about  $70.5^\circ$  relative to each of the other two ion guns. This corresponds to the arrangement shown in Figs. 3A and 3B where  $\alpha$  is about  $70.5^\circ$ ,  $\alpha'$  is about  $70.5^\circ$  and  $\theta$  is about  $55^\circ$ .

#### Example IV

A (001)<100> YSZ surface is formed using four ion beams as follows.

The process of Example I is followed except that four ion guns are provided. Each ion gun is about  $70.5^\circ$  apart from each of the two adjacent ion guns. The first two ion guns are about  $110^\circ$  apart, and the third and fourth ion guns are about  $110^\circ$  apart. This corresponds to the arrangement shown in Figs. 4A and 4B where  $\alpha$  is about  $70.5^\circ$ ,  $\alpha'$  is  $70.5^\circ$ , and  $\theta$  is about  $55^\circ$ .

#### Example V

A (001)<100> YSZ surface is formed using two ion beams as follows.

The process of Example I is followed except that the ion guns are not active simultaneously. Instead, the ion guns are used in series. Each ion gun is activated for a finite period of time.

#### Example VI

A (001)<100> YSZ surface is formed using two ion beams as follows.

The process of Example II is followed except that the ion guns are not active simultaneously. Instead, the ion guns are used in series. Each ion gun is activated for a finite period of time.

#### Example VII

A (001)<100> YSZ surface is formed using three ion beams as follows.

The process of Example III is followed except that the ion guns are not active simultaneously. Instead, the ion guns are used in series. Each ion gun is activated for a finite period of time.

#### Example VIII

A (001)<100> YSZ surface is formed using four ion beams as follows.

The process of Example IV is followed except that the ion guns are not active simultaneously. Instead, the ion guns are used in series. Each ion gun is activated for a finite period of time.



Example IX

A (001)<100> ceria surface is formed using two ion beams as follows.

Each of two ion beams is provided at an angle of about 45° to the perpendicular of a noncrystalline ceria surface. The two guns are about 90° apart. This corresponds to the arrangement shown in Figs. 2A and 2B where  $\alpha$  is about 90° and  $\theta$  is about 45°. The surface of the noncrystalline ceria material is heated to a temperature of from about 700°C to about 800°C after which the two ion guns are activated so that the surface of the noncrystalline ceria material is simultaneously exposed to ions from the ion guns. The ion guns are operated at 300 eV each with a beam current of from about 10 microAmperes per square centimeter to about 100 microAmperes per square centimeter. Ion texturing is performed for a time period of from about 30 seconds to about 90 seconds. This results in a (001)<100> ceria textured layer of about 20 nanometers in thickness and having a FWHM X-ray phi scan value of less than about 10°.

Example X

A (001)<100> MgO surface is formed using two ion beams as follows.

Each of two ion beams is provided at an angle of about 45° to the perpendicular of a noncrystalline MgO surface. The two guns are about 90° apart. This corresponds to the arrangement shown in Figs. 2A and 2B where  $\alpha$  is about 90° and  $\theta$  is about 45°. The surface of the noncrystalline MgO material is heated to a temperature of from about 700°C to about 800°C after which the two ion guns are activated so that the surface of the noncrystalline MgO material is simultaneously exposed to ions from the ion guns. The ion guns are operated at 300 eV each with a beam current of from about 10 microAmperes per square centimeter to about 100 microAmperes per square centimeter. Ion texturing is performed for a time period of from about 30 seconds to about 90 seconds. This results in a (001)<100> MgO textured layer of about 20 nanometers in thickness and having a FWHM X-ray phi scan value of less than about 10°.

Example XI

A (011)<100> YSZ surface is formed using two ion beams as follows.

The process of Example II is followed except that the first ion beam is at an angle of about  $35^\circ$  relative to the perpendicular of the noncrystalline YSZ surface and the second ion beam is at an angle of about  $35^\circ$  relative to the YSZ surface. The two guns are at an angle of about  $70.5^\circ$  relative to each other. This corresponds to the arrangement shown in Figs. 2A and 2B where  $\alpha$  is about  $110^\circ$ ,  $\theta_1$  is about  $35^\circ$  and  $\theta_2$  is about  $35^\circ$ .

It is to be understood that in any of the foregoing examples, layers can be deposited onto the ion textured surface. Such layers include, for example, a protective layer (e.g., a layer of material that is chemically compatible with a superconductor material or a precursor thereof, such as ceria,  $\text{LaAlO}_3$  or  $\text{SrTiO}_3$ ) or a layer of a superconductor material or a precursor thereof (e.g., a layer of a rare earth barium copper oxide, such as YBCO, or a precursor thereof, such as a halide-containing precursor).

While certain embodiments have been described, the invention is not limited to these embodiments. Other embodiments are in the claims.